2014-01-29

DRDC-RDDC-2014-L22

Produced for: PMO AOPS, Distribution List

Scientific Letter

Review of Anti-Icing/Ice Release Systems

Ice can build up rapidly on ships operating in cold climates, decreasing ship stability, equipment performance, and personnel safety, and increasing the resource allocation required to reduce the ice burden. With the requirement for the Royal Canadian Navy to patrol the Arctic Ocean, future Arctic Offshore Patrol Vessels, AOPS, will require technology for reducing the effects of icing events. This letter reviews the current state of the art in commercially available ice reduction coating systems.

Considerations

Ryerson of the US Army Corp of Engineers has produced some excellent reviews on ice management [1,2,3]. Ice accumulation on a ship can reduce stability, impair equipment operation and is hazardous to personnel safety. Ice accumulation on ships is estimated to arise 90 percent from spray and 10 percent from atmospheric icing. Atmospheric icing arises from fog, rain and snow, while spray comes from breaking waves, and mostly from the action of the ship plunging into waves. As the bow encounters a wave, water is lofted and air is entrained, creating a spray. Wind can carry the lofted water/spray across the ship when the wave's height exceeds the deck height. The temperature of the water in the spray will fall with the distance travelled, and may remain liquid until it makes contact with some part of the ship which then conducts heat away from the water. Seawater must reach at least -1.8° C to freeze, due to the salt content. Ship and wind speed, temperature, and wave height all contribute to icing rates [3].

Ship design also plays an important role in the degree of icing and the ability to deice the structure once icing has occurred [4]. Clean decks with few protrusions and maximum drainage can reduce icing locations and improve the ability to remove ice. A flared bow can reduce spray lofting and composite masts can reduce ice accretion on lattice work where it is difficult to remove. Composite masts can also shield antennas from ice buildup. Ice can be removed from composite structures by heating with warm air or through the use of conductive carbon fibres in the composite. Some of these features can be seen in Danish and Norwegian Ship Design, Figure 1, where anchoring equipment is below deck, railings and cables are minimized and boats are stored internally or covered.

A number of technologies have been identified for reducing icing once it has occurred, including design, the use of chemicals, coatings, heat (electrical, hot air and water, infrared, millimeter waves), expulsive systems, hydraulic and steam lances, mechanical force, piezoelectric actuators, pneumatic boots, and vibration [3,5]. Traditionally manual methods have been used for ice removal, though at a risk to personnel and equipment. Shipping rules for polar vessels require heating systems for decks, walkways, and superstructure which the US Navy has shown

for a Green Arctic Patrol Vessel can be supplied by waste heat recovery from engine exhaust [6]. A range of ice reducing/de-icing systems may be required for reducing ice accretion in all locations.

Figure 1: *Top left, Danish Knud Rasmussen Class [7], top right, Norwegian Svalbar Class [8], bottom, Danish Thetis Class [9].*

Water/Ice-Surface Interactions

Prevention of ice accretion, or anti-icing, and reducing the energy required to remove ice once it has formed are two factors that need to be considered for anti-icing and ice release coatings. For the following discussion water droplets from spray are considered. When a droplet contacts a surface adhesive forces will either hold the droplet in place, or if it is on a sloped surface and the gravitation force is greater than the adhesive force the droplet will roll away. No icing will occur if the droplet rolls away before it freezes. The equilibrium work of adhesion, W_{ad}, for a droplet to a smooth horizontal surface is given by the Young-Dupré equation

$$W_{ad} = \gamma_{LV}(1 + cos\theta) \qquad \text{EQ 1}$$

where γ_{LV} is the liquid-vapour surface tension, and θ is the contact angle. The contact angle is the angle between the solid-liquid and liquid-vapour interfaces, Figure 2, and is defined by

$$\cos\theta = \left(\gamma_{SV} - \gamma_{SL}\right)/\gamma_{LV} \qquad \text{EQ 2}$$

where γ_{SL} and γ_{SV} are the solid-liquid and solid-vapour surface tensions, respectively.

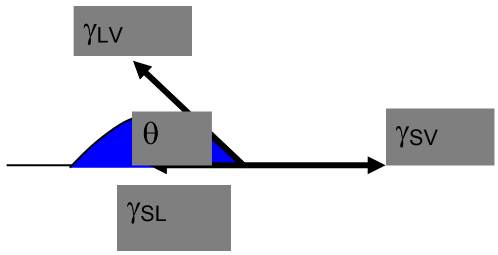

Figure 2: *Surface tensions for a liquid drop on a surface [10].*

The work of adhesion is the sum of the energy required to separate the solid and liquid plus the energies of formation of the new solid and liquid surfaces. The degree to which a liquid adheres to a surface will depend on the chemistry of the surface and liquid. Water has a high capacity to form hydrogen bonds and adheres well to surfaces with polar groups. Bare metals such as steel or aluminum are covered in thin layers of metal oxides and hydroxides which are polar and therefore water can hydrogen bonds to it. Thus water adheres strongly to and wets polar surfaces with a small contact angle and large work of adhesion. Such surfaces are said to have high surface energy. Surfaces which contain non-polar groups such as alkanes or perfluoroalkanes, adhere through van der Waals forces which are not as strong, and the surface is said to have low surface energy. When water is in contact with non-polar surfaces, the water-vapour surface tension is larger than the solid-liquid surface tension, so the water beads up with a large contact angle and small work of adhesion.

The maximum contact angle for a smooth surface is thought to be 120 degrees. Higher apparent contact angles are available if surfaces with micro and nanoscale roughness are formed. These surfaces trap a layer of air underneath the liquid which rests on the peaks of the surface roughness. If the surface is made from low surface energy materials, then the small area of liquid contact and high contact angle will enable water to roll away with only a small tilt to the surface. These materials are said to be superhydrophobic and tend to be fragile, Figure 3. Note if the water completely wets the surface then the adhesion energy can be much higher due to the increase in surface area.

Figure 3: *Water drops on a superhydrophobic coating [11].*

Freezing of a drop will depend on the air, water and substrate temperatures, liquid volume, and the heat capacity and conduction of the materials. Once the water has frozen and coated the surface, the ability to remove it will depend on the work of adhesion of ice to the surface. A recent study of smooth coatings has shown that the work of adhesion of ice to a coating correlates strongly with the liquid work of adhesion and the receding contact angle [12].

$$W_{ad-ice} \propto (1 + cos\theta_{rec}) \qquad \text{EQ 3}$$

The receding contact angle, θ_{rec} of a liquid drop would be the angle formed as the liquid pulls away from a surface. Receding angles can be measured by tilting a surface. The implication is that the work required to shear ice from a surface can estimated based on the measured properties of the water on the surface, and is smallest for the largest contact angle. Hence materials with low surface energy will also be the most effective as ice release coatings.

Anti-icing/Ice-Release Coatings

First it is observed that no coating will stop ice accretion, though some will reduce the accretion rate. It is also noted that coatings designed for use in mitigating the effect of icing fall into several categories. These include:

- Topical Applications: where low surface energy polymers or oils are rubbed into the surface of an existing corrosion protection coating. The effect is that the surface energy is reduced, surface roughness may also be reduced, and the additive may have lower surface adhesion strength than the ice does, thus facilitating shear. It has been found that such treatments depend on the chemical nature and condition of the substrate to which they are applied [1]. These types of coatings tend to be depleted with environmental exposure and may require frequent application.
- Ablative or Depletion Coatings: where the coating fails cohesively as ice is sheared away, or where low surface energy or oily additives leach to the surface and disrupt bonding. The effectiveness of these coatings will decrease with age.
- Low surface energy and flexible coatings. Use of silicone rubber with low surface energy and a degree of flexibility may help shear the ice. Fluorinated coatings reduce the surface energy.
- Superhydrophobic coatings.
- Other: Phase change materials that change shape/volume may reduce the adhesive strength of the ice-coating bond.

Literature reports of coating systems in actual use for mitigation of icing are limited. Ship rules and guidance documents indicate that coatings should be considered as one of the systems for ice management and may be used with other systems to reduce icing, improve ice release and energy efficiency [3,5,6,13]. In 1988, the US Navy published a list of coatings that could reduce icing and increase ice release, including polysiloxanes, fluorocarbons and what appears to have been a superhydrophobic coating [14]. For airplanes silicones and perfluoralkyl groups were identified as being potentially useful for reducing ice adhesion while Teflon containing coatings provided hydrophobic surfaces but porosity resulted in high adhesion [15,16,17]. None of the coatings mentioned appear to be in current production.

In 2003 for the purpose of reducing the icing of lock systems in winter, Ryerson measured the adhesion energy of ice to various materials and coatings using the zero degree cone test [3]. As reference materials, bare carbon steel and aluminum had adhesion strengths of 1414 kPa and 1575 kPa, respectively and Teflon 237 kPa. A number of the systems trialed produced ice adhesion strengths below that of bare metal though none were as low as Teflon. Some of the better performing coatings that were tested are presented in Table 1. Two observations were made: first repeat testing of the ice adhesion showed marked difference for some coatings. For instance the ice adhesion strength for Polysiloxane PSX-700 increased while for Inerta 160 it decreased. It was also observed that the performance was dependent on the substrate to which the coating was applied. The topical application Kiss-Cote as an example was effective on some surfaces and not others, and results indicate that it had eroded away after a six month exposure period. The conclusion of this work was that icephobic materials reduce the adhesion strength of ice and therefore facilitate removal by other methods. Also coating systems need to be well tested and have their durability evaluated.

The Anti-icing Materials International Laboratory, AMIL, reported on the adhesion reduction factor, AFR, of coatings compared to bare aluminum with tests made using a centrifuge [18,19]. Topically applied greases produced the highest AFRs, a number of commercial coatings performed better than bare metal, but not as good as Teflon, while a Wearlon product performed better than Teflon, Table 2.

In later publications Ryerson listed a number of available coating systems for reducing water and ice adhesion, aimed at offshore platforms and Coast Guard ships, Table 3 (these publications consider many more points on ice reduction as well) [2,3]. Most of these coatings are commercially available, and a number have high technology readiness levels, TRLs, for the marine environment. The coatings listed include topical applications, coatings, ablative/depletion coatings, and superhydrophobic coatings. Durability of the materials is not extensively known, and may be limited for certain materials such as the topical applications. However, there may be niche applications for each type of coating, and some important areas include radomes, antennas and optical surfaces/windows. Ryerson repeatedly makes the comment that the coatings need to be trialed in appropriate environments, and for specific locations, especially for areas where a slippery coating may be a safety issue. The gold standard appears to be the NuSil product R-2180, however, this coating is heat cured and so can only be applied to smaller objects. Other room temperature vulcanizing, RTV, silicone products from NuSil appear to have very good properties. Ryerson included a number of superhydrophobic treatments, however, the TRL levels for these materials is lower than some other coatings [3]. Durability is probably the biggest issue with superhydrophobic coatings, though recent research is promising [20,21].

Finally Ryerson listed a risk analysis which is useful for considering the most important areas for ice reduction, including in decreasing order of importance [3]:

- Seakeeping, Stability, Integrity, Functionality, Fire Stations, Life rafts;
- Antennas and Electronics, Deck Surfaces/Ladders;
- Cranes, Lifelines/Railings, Deck Machinery, and
- Boats, Hatches.

Table 1: *Coatings tested by the Army Corps of Engineers in order of increasing performance for first test [1].*

Material	Classification	Chemistry
Bare Metal		
Wearlon	Low surface Energy Coating	Methyl silicone epoxy copolymer
Inerta 160	Low Surface Energy Coating	Trimethyl hexamethylenediamine epoxy
PSX-700	Low surface Energy Coating	Siloxane and polyurethane epoxy
BMS 10-60		BMS (Boeing Material Spec) 10-60 polyurethane
Kiss-Cote	Topical	Polydimethyl siloxane
WC-1-ICE	Low Surface Energy Coating	fluoropolyol with PTFE and organofunctional silicone fluid additives,
Teflon	Low Surface Energy	Polytetrafluoroethylene (PTFE) thermoplastic

Table 2: *Coatings tested by AMIL in order of increasing performance for first test [20,21].*

Material	Classification	Chemistry
Bare Aluminum		
Lotusan	Superhydrophobic	
Preventex		
Tufram L4	Low Surface Energy Coating	Aluminum oxide in Proprietary Polymer
Staclean		
Airmax		
Ice Barrier		
CG2 Nanocoating	Superhydrophobic	Silica nanoparticles, oil and water repellent functional groups
Hang On		
Teflon	Low Surface Energy Material	
Wearlon anti-grafiti	Low Surface Energy Coating	Methyl silicone epoxy copolymer
Wearlon, Super F1-ICE	Low Surface Energy Coating	Methyl silicone epoxy copolymer
* No information provided in reports and blank spaces indicate no information available on the internet		

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Table 3: *Coatings reviewed by the Army Corps of Engineers in order of increasing performance for first test [2,3].*

Material	Classification	Chemistry	TRL*
Rain-X	Topical	SOPUS Products	5
FPU WC1 (ICE)™	Low Surface Energy	PTFE, Fluoroalkylsilane, and Dimethyl Siloxane in non-stick fluorinated polyurethane, developed by NRL and sold by 21st Century Coatings Inc.—Industrial and Marine Coatings, FPU WC15™ is enhanced.	8
AeroKret Coating [22]	Polysiloxane	A two layer coating consisting of an epoxy based primer, which bonds to most materials, followed by a flexible siloxane-based (Si-O-Si) nano-composite topcoat, Analytical Services & Materials Inc.	8-9
PCM Marine™	Low Surface Energy Coating-(ablative?)	Hydrophobic material coupled with a phase change material that expands and causes the material to break the substrate-ice bond, ePaint Company. Reports are that the coating surface is oily.	7+
ISurTec Nanotextured Super-hydrophobic Coatings	Superhydrophobic	Propietary photocrosslinker and nanotexture technology, Innovative Surface Technologies, Inc.	6
KISS-COTE	Topical	Polydimethyl siloxanesilicone-based polymer coating rubbed into the surface, KISS Polymers LLC.	7
PhaseBreak Flex MPD	Ablative, Low Surface Energy, Melting Point Depressant	Silicone-based coating that contains a melting point depressant (MPD) which relies on the hydrolysis of ethoxy silicates or titanates, MicroPhase.	8
HybridSil® Hydrophobic and HybridSil® Ice-phobic Coating	Superhydrophobic	Silica nanoparticles, oil and water repellent functional groups.	6
Shuttle Ice Liberation Coating (SILC)	Low Surface Energy, Ablative	A mixture of commercial Rain-X and 20 to 50% by weight Laurel Products Ultraflon MP-55 polytetrafluoroethylene (PTFE), NASA.	4
NuSil	Low Surface Energy Coating	Silicone RTV and Heat Cure. R-2180 heat cured coating has a very low adhesion strength, below that of Teflon. RTV cured NuSil coatings also have low adhesion strengths.	7 (8-9)
Anhydra coating	Superhydrophobic	Oceanit Laboratories, Inc.	4
NeverWet SE	Superhydrophobic	Ross Technology.	3
Hydro-bead	Superhydrophobic	Seashell Technology LLC.	6
* Based on transition to marine environment. Most are COTS products.			

Discussion

DRDC, Dockyard Laboratory Pacific, has been involved in minor studies of icephobic/ice release coatings. The lab has the capability to make zero degree cone test measurements, and has done so on ePaint's product PCM Marine™, Ecological Coatings EC 3800, and Interlac 1, used as the above water topcoat for the Canadian Navy. Panels coated with EC 3800 and Interlac 1, have been deployed on a Canadian Coast Guard ship in an icing environment. With promising results for reduced work required to remove icing. DRDC is also involved with New Zealand and the US through TTCP on an icephobic coating project which has been trialing the ePaint coating on a New Zealand Frigate. The lab has also been involved in the study of superhydrophobic materials, some of which show promise as anti-ice coatings.

The lists of icephobic coatings provided in this report are not exhaustive, and it is not known if some of the products listed, especially in Tables 1 and 2, exist, as they were not readily identified on the internet. All the coatings that are listed will not stop icing, though some will delay ice formation. The primary benefit from the coatings will be reduction of ice adhesion strengths, making it easier to clear ice manually or in conjunction with other de-icing technologies. In the case of thermal systems, the use of low surface energy coatings may reduce heating requirements, as might thermal conductive coatings.

Major factors to consider in these coatings are their durability and performance lifetime.

Conclusion

Anti-ice coatings are recommended for use in polar environments. A number of commercial-off-the-shelf coatings are available for anti-ice applications some with high technology readiness levels for the marine environment. Given the range of different products and technologies, some may be best suited for specific applications, such as glass coatings, antennas, radomes or composites. Other coatings may be too slippery for walkways, stairs and handrails. It is recommended that all coatings be environmentally tested so as to determine their durability to wear and environmental exposure, and to get an estimation of their effective life. It is recommended that trial coatings be applied in a number of locations on a ship(s) that will experience repeated icing events.

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